

## **How can plants influence tropospheric chemistry? The role of isoprene emissions from the biosphere.**

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In the context of global change, the study of tropospheric chemistry is of importance for two main reasons: air quality and climate. The relationship of chemistry to both is controlled by the same chemical processes and, in many cases, we are interested in the same species. For air pollution, we are concerned with the emission and formation of a suite of substances hazardous to human health, including ground-level ozone, peroxyacetyl nitrate (PAN, a powerful lachrymator), and particulate matter. For climate, we are chiefly interested in the processes that control the lifetime and distribution of reactive greenhouse gases, such as methane and ozone, as well as other agents of radiative forcing, such as aerosols.

Whilst all reactive compounds are interlinked through a vast array of complex chemical processes, for descriptive purposes tropospheric chemistry often takes ozone as its lynchpin. In situ formation of ozone depends on sunlight and on the relative levels of the oxides of nitrogen ( $\text{NO} + \text{NO}_2 = \text{NO}_x$ ) and volatile organic compounds (VOCs). Emissions of  $\text{NO}_x$  are largely from anthropogenic sources (for these experiments 78%), with the major fraction coming from fossil fuel combustion. Although there are significant anthropogenic sources of VOCs, it surprises many people to learn that emissions from the biosphere far outstrip—more than double—them on a global scale. Plants emit VOCs for many reasons, among them chemical protection, regulation, hormonal signaling, and reproduction. As an example of this, ethylene (ethene) is released by plants to stimulate opening of flowers, ripening of fruit, and shedding of leaves. Of the myriad of biogenic VOCs emitted into the atmosphere, isoprene is the major chemical species with an estimated source roughly equivalent to that of methane.

Present day global emissions estimates are valued at approximately 500 Tg (Lathière *et al.*, 2005; Guenther *et al.*, 2006.) For an amusing comparison, this is roughly equivalent to the weight of all human beings on the globe being emitted into the atmosphere each year.

Isoprene compliments its large emissions with high reactivity, having an atmospheric chemical lifetime of the order of minutes to hours, compared with approximately 9 years for methane. Its chemical reactivity arises from its structure: isoprene is a small molecule with two readily accessible double bonds. Importantly, oxidation of isoprene can form products that can transport NO<sub>x</sub> away from emission sources (e.g. PAN) and formaldehyde, which can be seen from space and act as a tracer of isoprene emissions (Palmer *et al.*, 2003); Figure 1 shows satellite measurements of HCHO. Isoprene chemistry can also have an indirect impact on the climate, both through its influence on ozone formation and through the consumption of hydroxyl radical (OH), the 'atmospheric detergent' responsible for removing many trace gases including methane. Furthermore, recent evidence from the field and the laboratory suggests that isoprene chemistry can contribute to aerosol formation (von Donkelaar *et al.*, 2007; Böge *et al.*, 2006).

Global change complicates the picture even further. Changing the meteorology alters the rate of chemical reactions and the distribution of the reacting species, through winds and changed frequencies of precipitation events that remove soluble compounds. Perturbations to meteorological parameters are also of importance for isoprene emission. Several experiments have suggested a positive dependence of isoprene emissions on temperature and radiation, and

others have pointed to the importance of ambient CO<sub>2</sub> level and water availability (Rosenstiel *et al.*, 2003; Pegoraro *et al.*, 2005; Sharkey *et al.*, 1996.) Vegetation modelers have assimilated empirical representations of these dependencies to derive isoprene emission estimates out to the year 2100 (Lathière *et al.*, 2005; Guenther *et al.*, 2006.)

In this paper, we will discuss the importance of including isoprene chemistry and emissions for simulating tropospheric chemistry. We use the United Kingdom Chemistry and Aerosol (UKCA) model to compare the results of simulations with and without isoprene, reporting on the impact on ozone as well as the lifetime of methane. We have also conducted other simulations where we have looked at potential future impacts of changing isoprene emissions, although the reader is directed towards our other papers (Zeng *et al.*, 2008; Young *et al.*, in press.)

## **Model description**

UKCA is a chemistry sub-model embedded in the Unified Model (UM), which is maintained by the Met Office for both research and numerical weather prediction. The 60 level version of the UM (version 6.1), which extends to a height of 84 km, is employed here with a horizontal resolution of 3.75 by 2.5 degrees. Model meteorology is forced using assimilated observations of present day sea surface temperatures (Rayner *et al.*, 2003).

The model chemistry simulates O<sub>x</sub>, HO<sub>x</sub>, and NO<sub>x</sub> cycles as well as the oxidation of methane, ethane, and propane. This chemistry package has been used in the chemistry transport model TOMCAT (Law *et al.*, 1998) and in UM4.5

(Zeng and Pyle, 2003). Additionally, isoprene oxidation is included using the condensed Mainz Isoprene Mechanism (Pöschl *et al.*, 2000). The model has 132 chemical reactions and 60 chemical tracers. More technical details can be found in Morgenstern, *et al.* (2008).

Isoprene emissions are derived using the Sheffield Dynamic Global Vegetation Model (SDGVM), which is forced by temperature, precipitation, and humidity from the Unified Model. The distribution of anthropogenic managed crop land is taken into account by applying a map of crop fraction from **SOURCE**. The SDGVM is allowed to run around these fixed areas of anthropogenic agricultural and pastoral influence, and then assigns plant functional types (a representation of ecosystem classifications) to individual grid cells. Plant functional types are calculated based on a number of factors, including given meteorological parameters, soil moisture, photosynthetically active radiation, and available nutrients. When vegetation has come to equilibrium in the model, the distribution is used as input to the Model of Emissions and Gases from Nature (MEGAN), which estimates isoprene emissions for input into the climate-chemistry model UKCA (Guenther, *et al.*, 2006; Lathière, *et al.*, 2008).

### **Impact on Ozone**

Figure 2 shows the geographical location and magnitude of present day isoprene emissions output from MEGAN for January and July, when peak emissions in the southern and northern hemisphere are largest, respectively. A meridional seasonality appears in the emissions that follows the path of the sun, as emissions of isoprene are closely correlated to radiation and temperature.

Tropical rainforests are notably high emitting, and key emission regions include the Amazon, central Africa, Southeast Asia, and in July, the southeast of the United States. It is also important to note that isoprene emissions are regionally localized, and that any downwind or large scale effects therefore must involve photochemical processing.

Figure 3 shows the dramatic effect that including isoprene has on the model on ozone and PAN. Recall that the production of ozone depends on the concentration of  $\text{NO}_x$  and VOC in a highly non-linear way. By including isoprene, the spatial distribution of surface ozone is dramatically altered, changing by over 50% in certain regions. In January, the three main regions of high emission all show a decrease in surface ozone concentrations when isoprene is included in the model. In these areas PAN also increases, and the correlation between PAN and decreased surface ozone indicates that  $\text{NO}_x$  is being “locked up”. This means that when isoprene is included, more PAN is formed, and this reduces the production of ozone by removing one of the ingredients ( $\text{NO}_2$ ) necessary in its formation.

In July, the same relationship between high emitting regions and decreased surface ozone appears with the major exception of southeastern United States. In this area, which is rich in anthropogenic pollutants such as  $\text{NO}_x$ , the addition of isoprene (or other reactive VOC) leads to dramatic increases in ozone production. The same is true in Europe, where isoprene increases are less pronounced (see Figure 2), but nonetheless ozone concentrations increase over 10%. In these  $\text{NO}_x$ -rich regimes, where ozone production was previously limited by a lack of VOC, the addition of isoprene dramatically increases ozone production.

In South America, a bimodal distribution of changes in ozone appears over the Amazon. In the more heavily populated southeastern part of the continent, where ozone increases,  $\text{NO}_x$  emissions are much higher than in the north. To compound this, isoprene emissions increase more significantly in the north while remaining relatively similar in the south. In the northern, VOC saturated environs, too much VOC can tip the ozone production away from a maximum as self reactions and other loss mechanisms begin to have an effect. Outflow areas from this northern region show a considerable increase in PAN formation, and decomposing PAN leads to an increase in ozone of over 30% over the equatorial Pacific ocean. Here, photochemical processing plays a key role and leads to major changes at great distances away from the region of direct perturbation.

Figure 4 shows zonal mean plots of ozone for runs with and without isoprene. Interestingly, changes to surface emissions have a significant effect higher up in the atmosphere. In the tropics, ozone decreases with the addition of isoprene, which is similar to the surface plots in Figure 3. In July, the northern hemisphere increase in ozone can be seen near 40N.

### **Impact on Methane**

Figure 5 shows the average annual seasonal cycle of methane lifetime in the atmosphere for simulations with and without isoprene emissions. Two things are notable about this image, the first of which is the significant seasonal cycle of methane lifetime, arising from the fact that OH concentrations are elevated in the northern hemisphere summer. This is due to higher ozone concentrations; ozone is required in the formation of OH via photolysis. An increased abundance of

ozone and of the anthropogenic pollutant  $\text{NO}_2$  also leads to an increase in OH recycling, further reducing  $\text{CH}_4$  lifetime in the these areas.

The second is the difference in Figure 5 between the runs with and without isoprene. The average annual methane lifetime for these runs is 10.2 (without isoprene) and 12.5 (with). Isoprene therefore accounts for a 22.5% increase in the methane lifetime due to its rapid chemical reaction with OH. The hydroxyl radical forms the largest sink for atmospheric methane, and its interaction with isoprene effectively prevents it from reacting, and therefore removing, methane.

Interestingly, the magnitude of the seasonal cycle also increases when isoprene is included in model calculations. As isoprene emissions are largely located in the southern hemisphere (see Figure 2), the removal of OH due to chemical reaction isoprene is more marked than in the northern hemisphere. In the northern hemisphere summer, ozone increases significantly with the inclusion of isoprene. Increased ozone, along with increasing radiation due to the season leads to higher values of OH. Two competing factors are at play here: first, the direct interaction between OH and isoprene, and second, the indirect effect of isoprene in the formation of ozone, which in turn leads to altered concentrations of OH.

The direct impacts of isoprene on OH can be seen in Figure 6. In January, when isoprene emissions are concentrated in the unpolluted southern hemisphere, global OH concentrations decrease. This is due to the first factor, direct chemical reaction between isoprene and OH. In contrast, OH increases in July when isoprene is included in the model. Although direct chemical reaction with OH is still occurring, it is overwhelmed by the second, indirect effect, namely



the chemical production of ozone, which leads to higher OH values through photolysis.

### **Conclusion**

These two experiments have shown that in order to simulate ozone concentrations in the atmosphere accurately, a decent representation of emissions from the biosphere must be included. The inclusion of isoprene emissions significantly impacts the distribution and concentration of atmospherically relevant trace gases such as ozone and methane. Biosphere-atmosphere coupling is thus key in our understanding of future global change.

Furthermore, while natural feedbacks between radiation, temperature, emissions, and atmospheric chemistry will play an important role in the future, anthropogenic impacts will also have an impact. Policy and business decisions about land use change and large scale crop change related to the implementation of biofuels, for example, is one way that we could influence the magnitude of isoprene and other VOC emissions globally. Knowing that isoprene has the ability to change ozone concentrations by over thirty percent only reinforces the scientific imperative that we study biosphere-atmosphere interactions.

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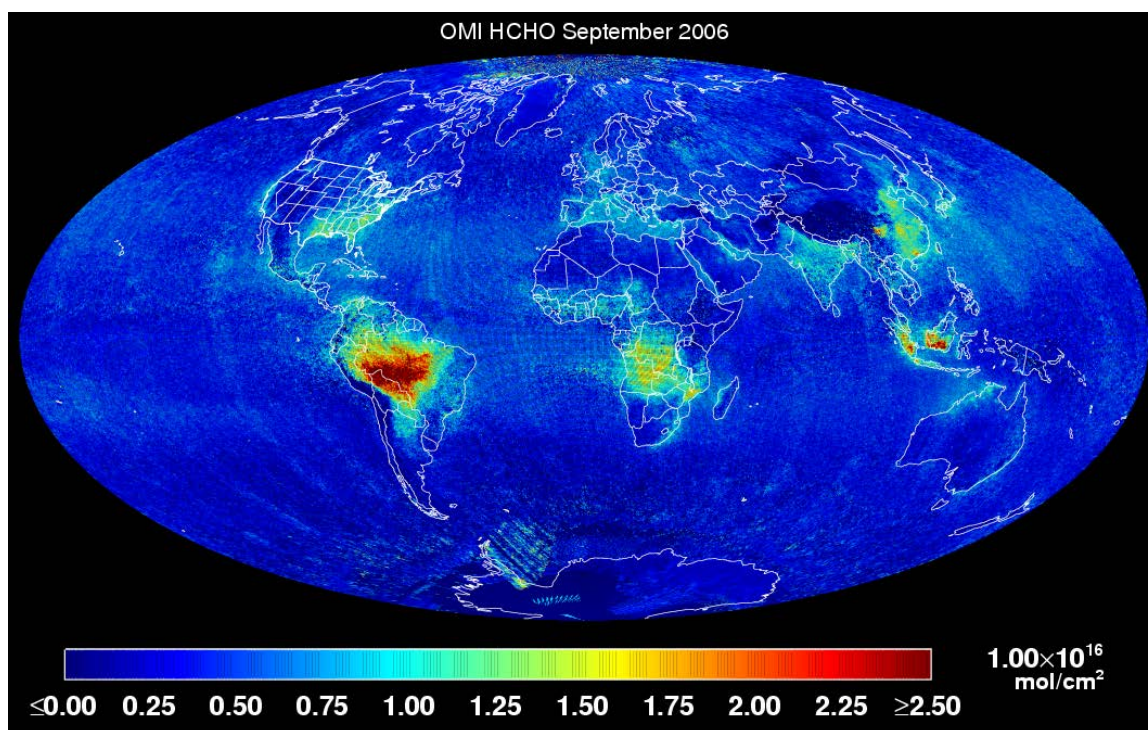
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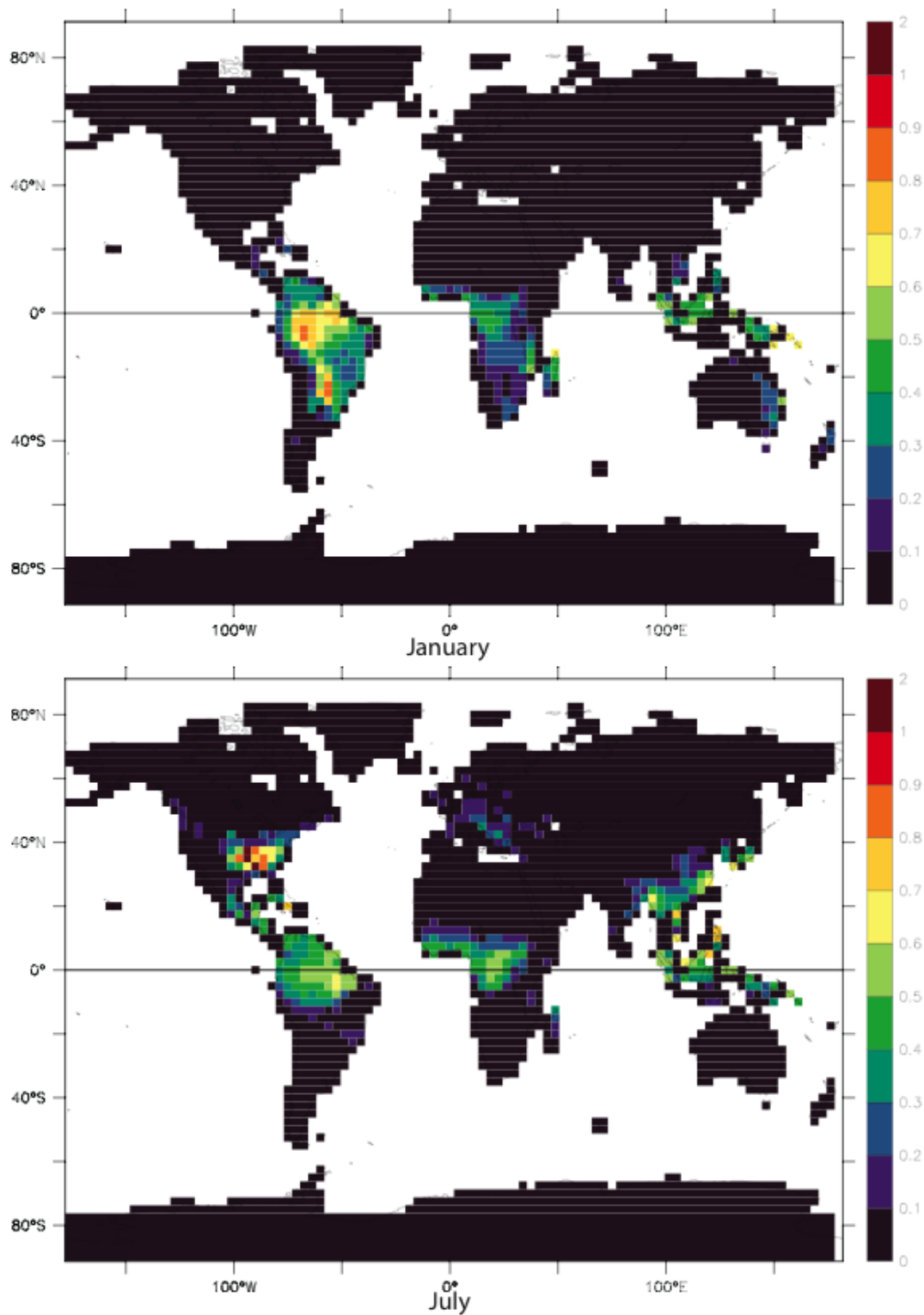
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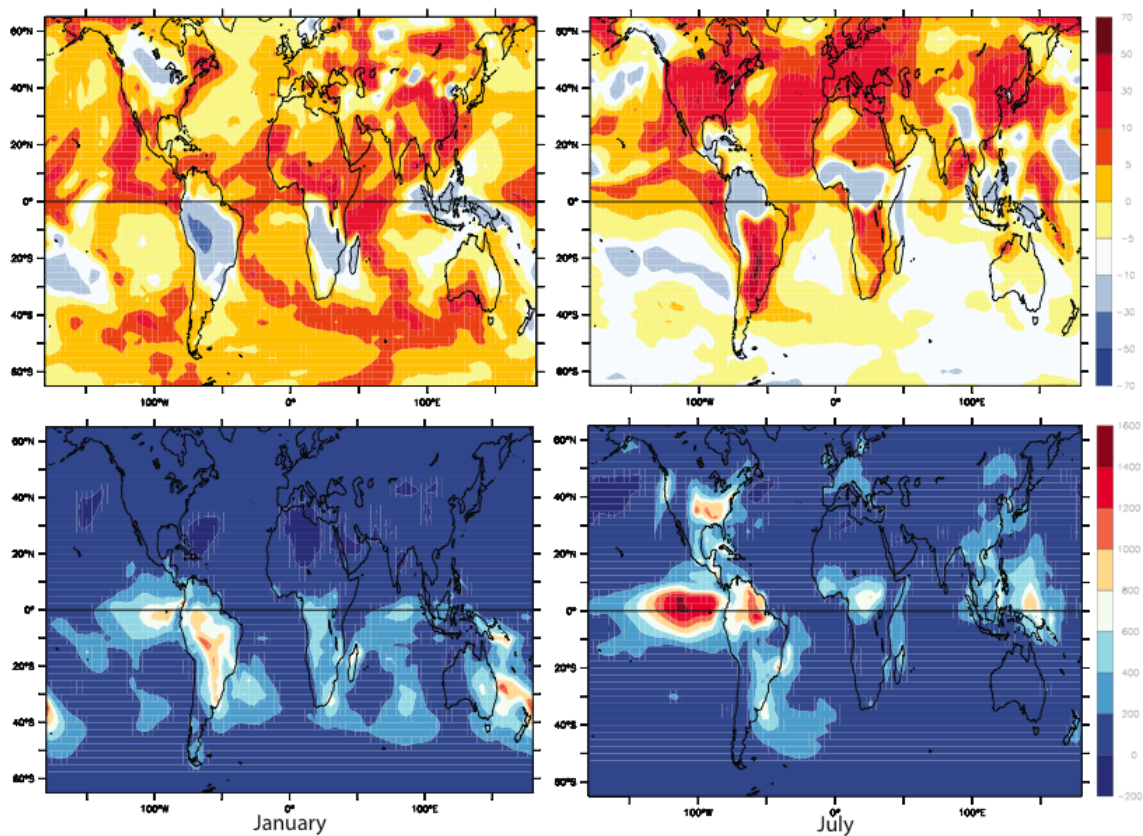
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**Figure 1.** Formaldehyde measurements from the Ozone Monitoring Instrument (OMI) satellite. Image from NASA, at <http://macuv.gsfc.nasa.gov/OMITraceGases.md>

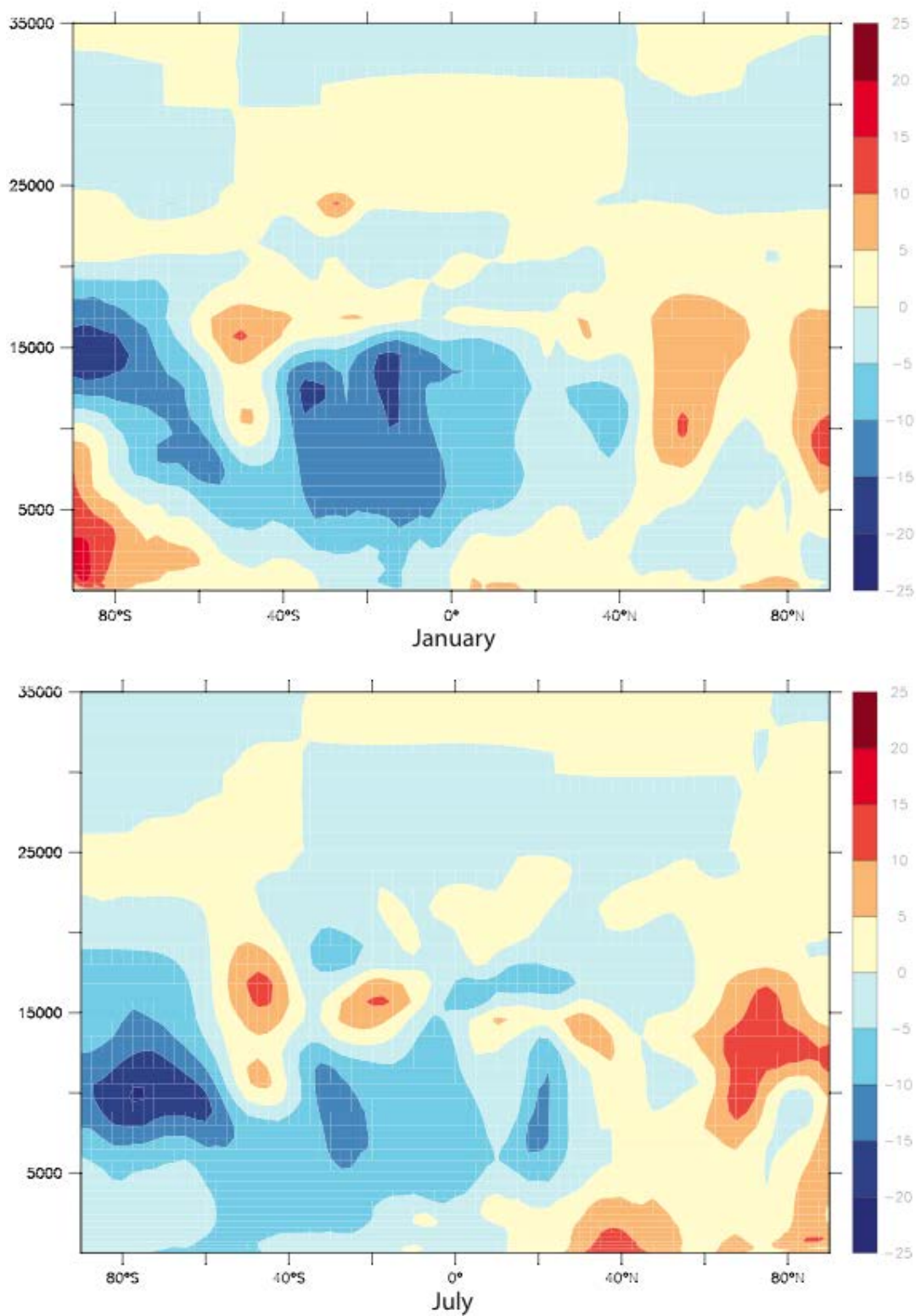


**Figure 2.** Isoprene emissions [ $\mu\text{g m}^2 \text{s}^{-1}$ ] for January and July.



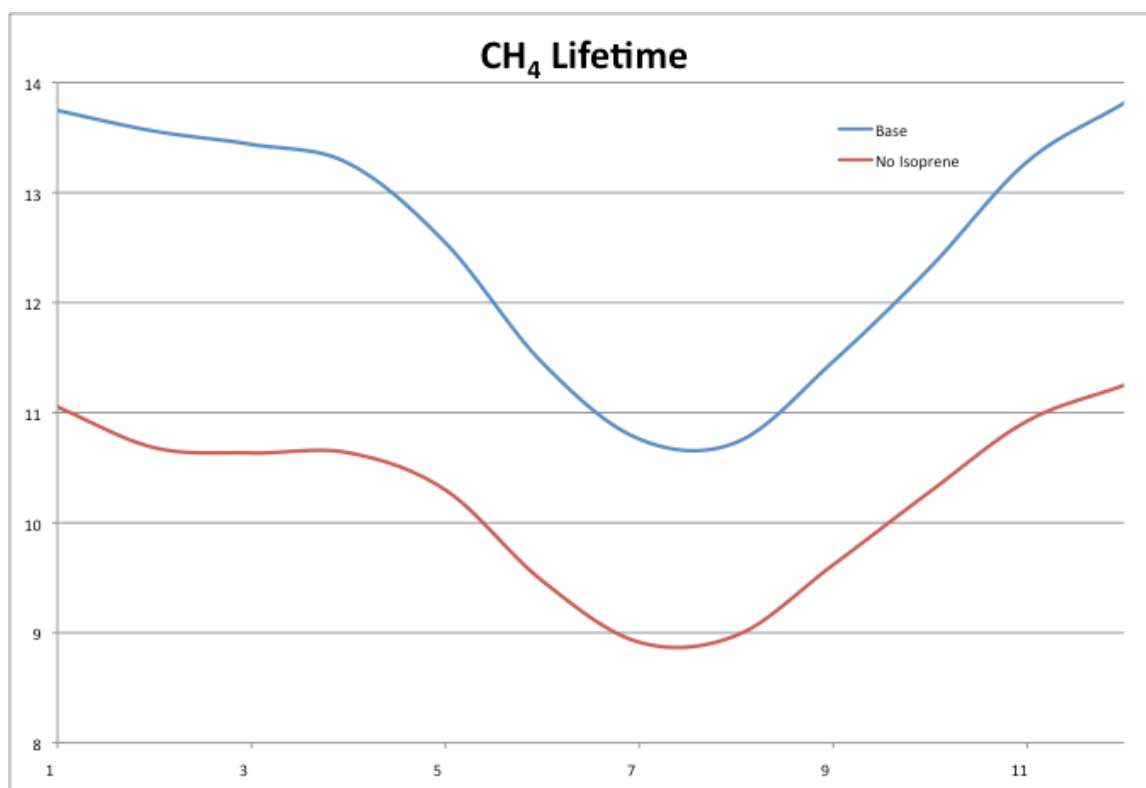
**Figure 3.** Relative change in five year average surface ozone (top) and PAN (bottom) concentrations for January (left) and July (right.)



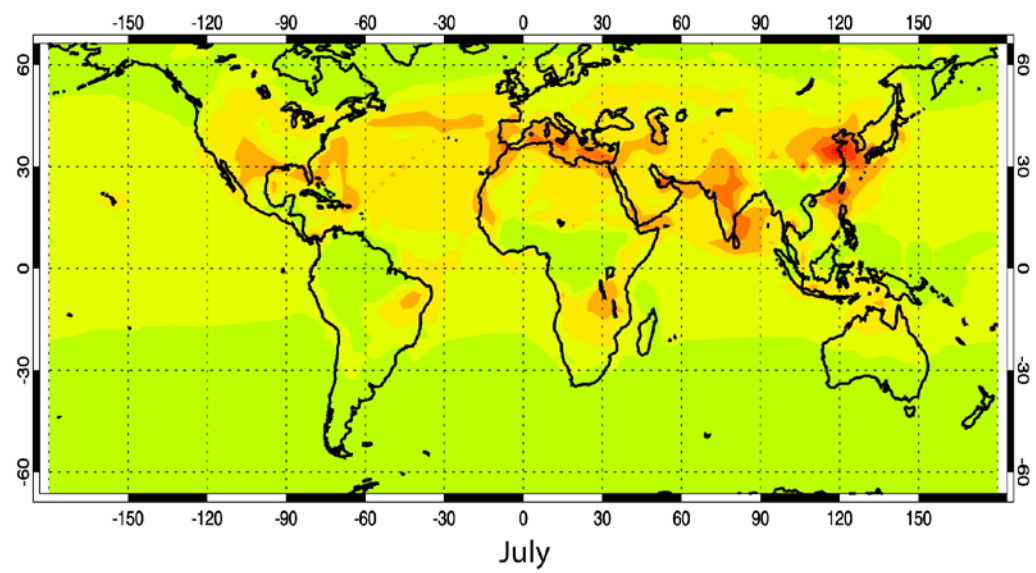
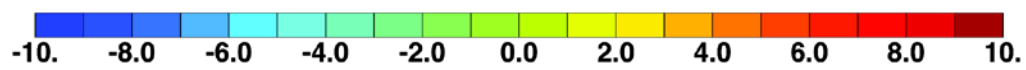
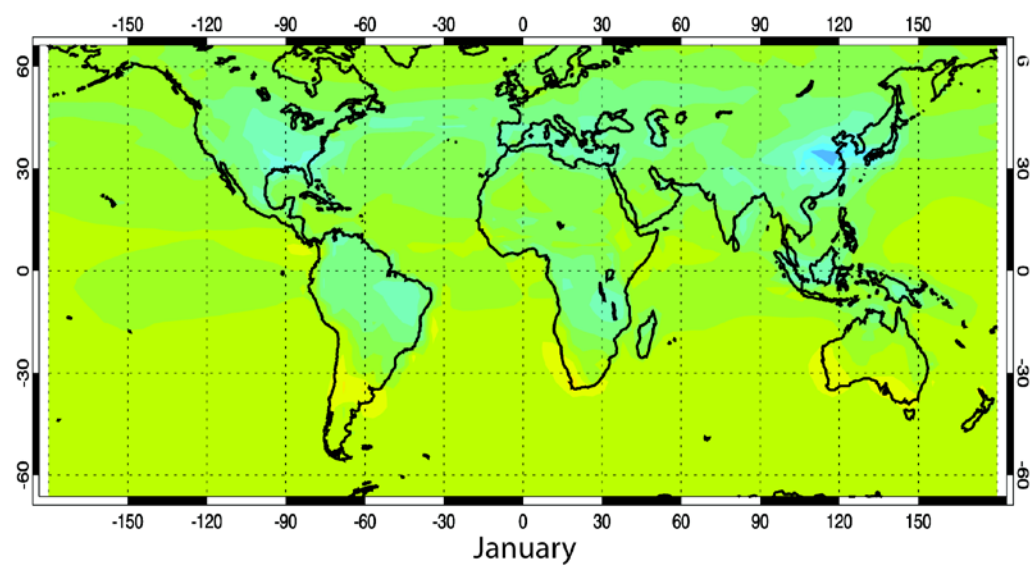


**Figure 4.** Relative change in five year average zonal mean ozone concentrations when isoprene is included in the model.





**Figure 5.** Seasonal variation in methane lifetime for simulations with (blue) and without (red) isoprene emissions.



**Figure 6.** Difference in OH [ $10^6$  molec  $\text{cm}^3$ ] when isoprene is included in the model.